



# Highly selective oxidation of glycerol over Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure: Dual reaction pathways induced by photogenerated <sup>1</sup>O<sub>2</sub> and holes

Shuai Zhao<sup>a</sup>, Zan Dai<sup>a</sup>, Wenjin Guo<sup>a</sup>, Fengxi Chen<sup>a</sup>, Yunling Liu<sup>b</sup>, Rong Chen<sup>a,\*</sup>

<sup>a</sup> School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430073, PR China

<sup>b</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

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## ABSTRACT

Selective oxidation of glycerol to produce aimed high-value added products is of great importance in chemical industry. Photocatalytic oxidation provides a promising and green strategy for selective glycerol oxidation. In this work, we develop a Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure via a facile solvothermal method for the selective oxidation glycerol to 1, 3-dihydroxyacetone (DHA) in water under visible light irradiation. The excellent performance in activity and selectivity of Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure for DHA production is attributed to a dual-pathway photocatalytic reaction process. The mass production <sup>1</sup>O<sub>2</sub> ascribed to the reduced energy gap (ΔE<sub>ST</sub>), the enhanced spin-orbit coupling (SOC) and the presence of oxygen vacancy is beneficial for the selective oxidation of glycerol to DHA. Simultaneously, the metallic bismuth in the heterostructure promotes the separation of photogenerated holes with efficient redox potential and facilitates the binding bismuth with ortho-hydroxyl in glycerol, thus enhancing the yield and selectivity of DHA production. This work provides a novel strategy and thorough understanding of the development of highly efficient bismuth-based photocatalyst for selective oxidation in organic reactions.

## 1. Introduction

As a primary by-product from the production of biodiesel, the surplus glycerol has brought about a series of problems [1,2]. Therefore, the economics and sustainable development of biodiesel production requires the integrated utilization of glycerol [3–5]. Generally, the selective oxidation of glycerol could generate numerous industrially high-value added products such as 1, 3-dihydroxyacetone (DHA), glyceraldehyde (GAD), glyceric acid (GCA), lactic acid (LA), glycolic acid (GCOA), and formic acid (FA) [6–11] *etc.* (Scheme S1, Supporting Information). Among them, DHA is one of most important products due to its potential use in fine chemical industry, particularly in pharmaceutical and cosmetics [12,13]. However, due to the presence of three reactive hydroxyl groups, the highly selective oxidation of glycerol to DHA still remains a big challenge [14,15]. Besides microbial oxidation via fermentation process [16,17], the selective oxidation of glycerol via heterogeneous catalyst (*i.e.* Pd, Pt, Au based bi-metallic catalysts) [18–20] and homogenous catalyst (*i.e.* C<sub>27</sub>H<sub>31</sub>F<sub>3</sub>IrN<sub>3</sub>O<sub>3</sub>S, C<sub>21</sub>H<sub>20</sub>F<sub>3</sub>IrN<sub>3</sub>O<sub>5</sub>S, [Cp\*Ir(IME)<sub>2</sub>Cl]BF<sub>4</sub>) [21,22] have been reported. Electrochemical approach has also realized the glycerol being

converted to DHA by using modified electrode [23,24]. Nevertheless, different obstacles such as long operation time, low selectivity and metal loss in the process are presented in their further applications. Currently, photocatalytic oxidation provides an appealing strategy for selective oxidation of alcohol and polyol [25]. For examples, selective glycerol oxidation to DHA was realized over flower-like Bi<sub>2</sub>WO<sub>6</sub> under visible light irradiation [26]. Selective oxidation of alcohol using Bi<sub>2</sub>MoO<sub>6</sub> as a photocatalyst also has been reported [27,28]. However, the unsatisfied photocatalytic performance of photocatalyst in selective glycerol oxidation still hinder the practical applications [29,30].

To overcome the obstacles of low photocatalytic efficiency and selectivity, the discovery or design of highly effective visible-light-driven photocatalysts for selective glycerol oxidation to DHA is particularly of great interest and importance. Recently, bismuth-based oxysalt has emerged as promising candidate owing to its unique layered structure and suitable valence band and conduct band position [31–33]. Moreover, previous works have demonstrated the presence of metallic Bi as a promoter has a significantly positive effect on the activity and selectivity of catalyst [34,35]. For instances, Ning and Garcia have previously reported some bismuth-modified noble metal catalysts, which

\* Corresponding author.

E-mail address: [rchenhku@hotmail.com](mailto:rchenhku@hotmail.com) (R. Chen).

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exhibited improved activity and selectivity of the oxidation of glycerol to DHA due to the geometrical effect caused by the blocking of Pt surface by Bi [36,37]. Unfortunately, the essential role of bismuth promoter in improving activity and selectivity of the composited catalyst is still no fully understood, especially in photocatalysis.

Motivated by these concerns, in this work, we have developed a Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure by a facile one-step solvothermal method for selective oxidation of glycerol to DHA under visible light irradiation. By utilizing the synergistic effect of metallic Bi and Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub>, it is believed that Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure might possess mild oxidation power for visible-light-driven photocatalytic selective oxidation of glycerol. To further elucidate the mechanism of the enhanced activity and selectivity over Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure, the dual reaction pathways of photocatalytic glycerol oxidation was proposed, which has not been reported in previous literatures.

## 2. Experimental

### 2.1. Materials

Bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) and sodium hydroxide (NaOH), glycerol, 1, 2-propylene glycol, 1, 3-propylene glycol, 1, 3-dihydroxyacetone (DHA) and 1,3-diphenylisobenzofuran (DPBF) were purchased from Aladdin (Shanghai, China). Tert butyl alcohol (TBA), ammonium oxalate (C<sub>2</sub>H<sub>10</sub>N<sub>2</sub>O<sub>5</sub>), carbon tetrachloride (CCl<sub>4</sub>), benzoquinone (BQ), sodium azide (NaN<sub>3</sub>), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O), ethanol and ethylene glycol (EG) were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used without further purification.

### 2.2. Preparation

In a typical procedure, 1.9403 g Bi (NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 0.4839 g Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O were dissolved into 10 mL of ethylene glycol (EG), respectively. Then the two solutions were mixed, followed by the addition of ethanol (20 mL) and sodium hydroxide aqueous solution (2 M, 6 mL). After vigorously stirring, the mixed solution was transferred into a 100 mL teflon-lined stainless steel autoclave to perform solvothermal process at 160 °C for 12 h. Subsequently, the autoclave was cooled down to room temperature naturally, and the obtained product was centrifuged and washed with ethanol for 5 times, then dried at 60 °C for characterization (**BMO-1**). Other samples (**BMO-2** ~ **BMO-4**) were prepared by using different amount of NaOH under identical experimental conditions. The experimental parameters are listed in Table 1.

### 2.3. Characterization

The composition and crystal phase were characterized by powder X-ray diffraction (XRD, Brukeraxs D8 Discover) with Cu Kα radiation of 1.5406 Å. The morphology and structure were characterized by scanning electron microscope (SEM, Hitachi S4800) operating at 10.0 kV and transmission electron microscope (TEM, JEOL JSM-2010) operating at 200 kV. X-ray photo-electron spectra (XPS) were performed on a VG Multilab2000 spectrometer by using Al Kα (1486.6 eV) radiation

**Table 1**  
The experimental parameters for the preparation of **BMO** samples.

Sample	Bi source	Mo source	NaOH	Composition
<b>BMO-1</b>	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	6 mL	Bi <sub>3.64</sub> Mo <sub>0.36</sub> O <sub>6.55</sub>
<b>BMO-2</b>	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	8 mL	Bi/Bi <sub>3.64</sub> Mo <sub>0.36</sub> O <sub>6.55</sub>
<b>BMO-3</b>	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	10 mL	Bi/Bi <sub>3.64</sub> Mo <sub>0.36</sub> O <sub>6.55</sub>
<b>BMO-4</b>	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	5 mL	Bi <sub>2</sub> MoO <sub>6</sub> /Bi <sub>3.64</sub> Mo <sub>0.36</sub> O <sub>6.55</sub>
<b>BMO-5<sup>a</sup></b>	Bi	<b>BMO-1</b>	—	Bi/Bi <sub>3.64</sub> Mo <sub>0.36</sub> O <sub>6.55</sub>

<sup>a</sup> The experimental detail was shown in Supporting Data.

as the source. UV–vis diffuse reflectance spectra (DRS) were measured by an UV–vis spectrophotometer (HITACHI UH4150) with BaSO<sub>4</sub> as a reference and were converted from reflection to absorbance by the Kubelka-Munk method. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained on a TENSOR 27 spectrophotometer manufactured by BRUKER Company (Germany). The steady-state fluorescence and phosphorescence spectra were obtained on a PE LS55 fluorescence spectrometer equipped with an integrating sphere (PH was recorded by accumulating 100 flash counts per point). The μs-domain time-resolved phosphorescence spectra and ns-domain time-resolved fluorescence spectra were obtained on an FLS980 fluorescence spectrometer (Edinburgh Instruments Ltd.). Photocurrent, electrochemical impedance spectroscopy and Mott-Schottky measurements were carried out on an electrochemical workstation with three-electrode (CHI-660E, China).

### 2.4. Evaluation of photocatalytic activity for glycerol oxidation

In a typical process, 10 mg catalyst was suspended in 3 mL of glycerol/H<sub>2</sub>O solution (65 mmol/L). The suspension was transferred into a custom-made Pyrex glass bottle and stirred for 30 min. The reaction solution was illuminated by a 125 W Xe lamp for 4 h. After the illumination, the mixture was centrifuged at 9000 rpm for 20 min to completely remove the catalyst particles. The remaining solution was analyzed with a High performance liquid chromatograph (HPLC, Agilent 1260LC). The chemical structures of the products were confirmed by LC–MS (Agilent G6520 Q-TOF LC/MS). The conversion of glycerol and selectivity of DHA was calculated by the following equations:

$$\text{Conversion(\%)} = [(C_0 - C_{\text{GLY}})/C_0] \times 100$$

$$\text{Yield(\%)} = C_{\text{DHA}}/C_0 \times 100$$

$$\text{Selectivity(\%)} = [C_{\text{DHA}}/(C_0 - C_{\text{GLY}})] \times 100$$

where C<sub>0</sub>, C<sub>GLY</sub> and C<sub>DHA</sub> was the initial concentration of glycerol, the concentration of the glycerol and DHA after photocatalytic reaction, respectively.

### 2.5. Reactive oxygen species (ROS) determination

Electron spin resonance (ESR) signals were examined with an electron spin resonance spectrometer (JES FA200) by using 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2, 2, 6, 6-tetramethylpiperidine (TEMP) as trapping agent. The settings for the ESR spectrometer were as follows: center field (3510.00 G), microwave frequency (9.79 GHz), and power (5.05 mW). The irradiation source was a 125 W xenon lamp. Tertiary butanol, ammonium oxalate, tetrachloromethane, benzoquinone and sodium azide were added to the photocatalytic glycerol oxidation system to detect the active species in the conversion process of glycerol under identical conditions.

## 3. Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) patterns of as-prepared samples (**BMO-1**, **BMO-2**, **BMO-3**), which displays good crystallinity. The distinct diffraction peaks of **BMO-1** correspond to pure cubic Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> phase (JCPDS 43-0446). However, it is found that additional diffraction peaks at 37.96, 39.62, 48.70, and 56.03 could be detected in the XRD patterns of **BMO-2** and **BMO-3**, which is well-indexed to rhombohedral Bi (JCPDS 05-0519). It is believed that the formation of metallic bismuth is owing to the weak reducing ability of EG [35]. We also found that the Bi content could be easily mediated by altering the NaOH concentration, which was verified by the stronger Bi diffraction peaks in **BMO-3** than that in **BMO-2**. Different chemical states of bismuth could be found in the deconvoluted high resolution Bi

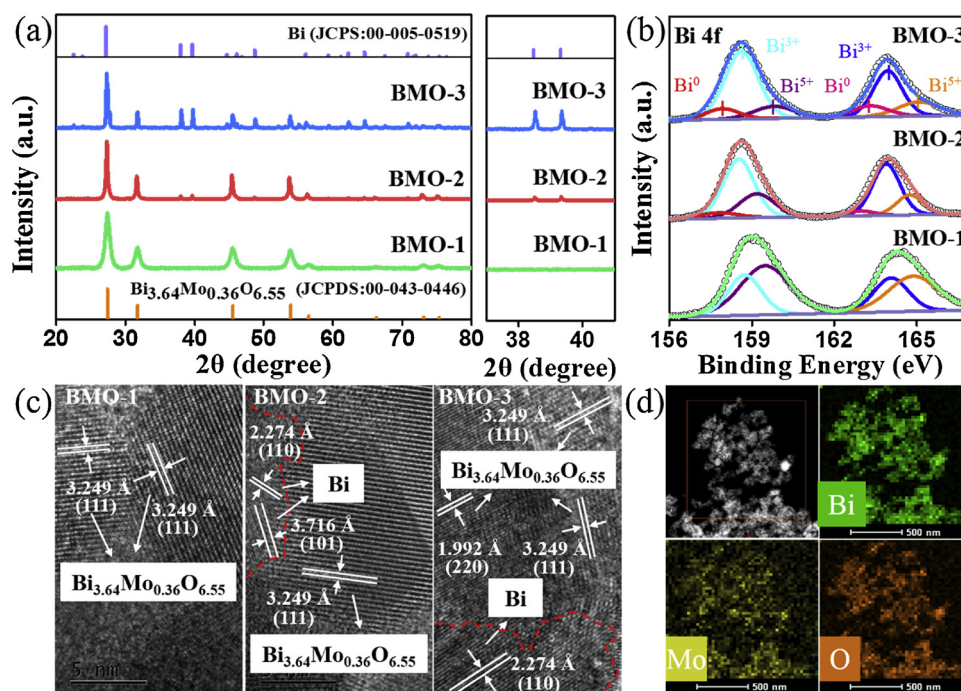


Fig. 1. Powder X-ray diffraction pattern (a), high-resolution Bi 4f XPS spectra (b), HRTEM images of **BMO** samples (c), and EDX mapping of **BMO-2** samples (d).

4f XPS spectra of **BMO** samples, as shown in Fig. 1b. The binding energies at 159.7, 165.1 eV and 158.6, 164.4 eV is attributed to Bi<sup>5+</sup> and Bi<sup>3+</sup> in Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub>, respectively [27]. And the peaks centered at 157.5 and 162.1 eV in XPS spectra of **BMO-2** and **BMO-3** are ascribed to metallic Bi, further demonstrating the formation of Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> composites [38].

All the **BMO** samples present uniform morphology of well-dispersed nanoparticles with the average size of 20 nm, as demonstrated by SEM and TEM images (Figure S1, Supporting Information). HRTEM images reveal the surface atomic arrangement of the as-prepared **BMO** nanoparticles (Fig. 1c). Two sets of characteristic lattice fringes of cubic Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> and metallic bismuth could be measured in HRTEM images of Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructures (**BMO-2** and **BMO-3**). The d spacing of 0.3249 and 0.1992 nm are indexed to (111) and (220) crystalline planes in Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub>, and the d spacing of 0.2274 and 0.3716 nm correspond to (110) and (101) planes of metallic Bi. Noticeably, the lattice fringes between metallic Bi and Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> contacted closely, indicative of the fabrication of the Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure. Only one set of lattice fringes of cubic Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> is observed in **BMO-1** sample, illustrating the pure phase of **BMO-1**. Moreover, the EDX mapping of **BMO-2** reveal that the bismuth is well-dispersed in Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> without aggregation (Fig. 1d).

Consequently, the photocatalytic ability of **BMO** samples for glycerol oxidation to DHA under visible light are determined. The conversion and selectivity of photocatalytic oxidation of glycerol is qualitatively analyzed by HPLC measurement (Figure S2, Supporting Information). As depicted in Fig. 2, Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructures (**BMO-2** and **BMO-3**) display obviously higher photocatalytic oxidation abilities than that of pure Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> sample (**BMO-1**), and **BMO-2** could oxidize 42.3% of glycerol within 4 h. While the glycerol conversion over **BMO-1** and **BMO-3** is 28.6% and 31.9%, respectively. More importantly, Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure could achieve high selectivity (97% ~ 99%) of converting glycerol to target product DHA. Compared with the reported catalysts in glycerol oxidation, Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure exhibits remarkably superior photocatalytic performance for the selective oxidation of glycerol to DHA, which is summarized in Table 2. To the best of our

knowledge, the simultaneously realization of high selectivity and high yield of glycerol oxidation to DHA has rarely been reported.

To understand the highly selective oxidation ability of Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure in the glycerol oxidation, the photocatalytic oxidation of glycerol over **BMO** samples are also performed in different atmospheres (Fig. 3a and b). It is found that the DHA yield is highly related to the involved O<sub>2</sub> in the glycerol oxidation, illustrating that the oxidation of glycerol involves in a photocatalytic oxygen activation process. Thus, electron spin resonance (ESR) measurement is used to determine the possible produced reactive oxygen species (ROS). As illustrated in Fig. 3c, both <sup>•</sup>O<sub>2</sub><sup>−</sup> and <sup>1</sup>O<sub>2</sub> could be generated in the presence of **BMO** samples upon light irradiation, and negligible <sup>•</sup>OH signals could be observed in the ESR spectra of all **BMO** samples. Specifically, **BMO-2** with highest photocatalytic ability of glycerol oxidation to DHA could yield highest <sup>1</sup>O<sub>2</sub> amount under identical conditions. While **BMO-1** possesses highest ability of generating <sup>•</sup>O<sub>2</sub><sup>−</sup> among **BMO** samples. As we known, <sup>1</sup>O<sub>2</sub> is one of the highly reactive oxygen species, which could act as a mild oxidant for selective oxidation [49–51]. Hence, it is believed that the highly selective oxidation ability of **BMO-2** for glycerol to DHA is closely related to the mass-produced <sup>1</sup>O<sub>2</sub>. Therefore, the scavenge experiments are carried out to clarify the contribution of <sup>1</sup>O<sub>2</sub> in the selective oxidation of glycerol to DHA. As shown in Figure S3 (Supporting Information), the pumping of N<sub>2</sub> obviously inhibits the production of DHA, illustrating the involvements of reactive oxygen species in the glycerol oxidation. The addition of TBA (<sup>•</sup>OH scavenger) and BQ (<sup>•</sup>O<sub>2</sub><sup>−</sup> scavenger) have slight influence on the DHA yield. However, the DHA yield decreases dramatically in the presence of NaN<sub>3</sub> (<sup>1</sup>O<sub>2</sub> scavenger), suggesting that <sup>1</sup>O<sub>2</sub> was the dominating reactive species for the photocatalytic oxidation of glycerol to DHA.

Due to the stronger oxidation ability of <sup>•</sup>O<sub>2</sub><sup>−</sup> than that of <sup>1</sup>O<sub>2</sub>, the peroxidation of glycerol usually would occur in the presence of <sup>•</sup>O<sub>2</sub><sup>−</sup>, which leads to the generation of other organic products, instead of DHA. Therefore, the little production of <sup>•</sup>O<sub>2</sub><sup>−</sup> over **BMO-2** had no influence on the selective oxidation of glycerol to DHA. To verify this, Bi<sub>2</sub>MoO<sub>6</sub>/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure (**BMO-4**) with more generated <sup>•</sup>O<sub>2</sub><sup>−</sup> radicals is prepared (Figure S4, Supporting information). Compared with **BMO-2**, the dominated <sup>•</sup>O<sub>2</sub><sup>−</sup> produced in **BMO-4** would

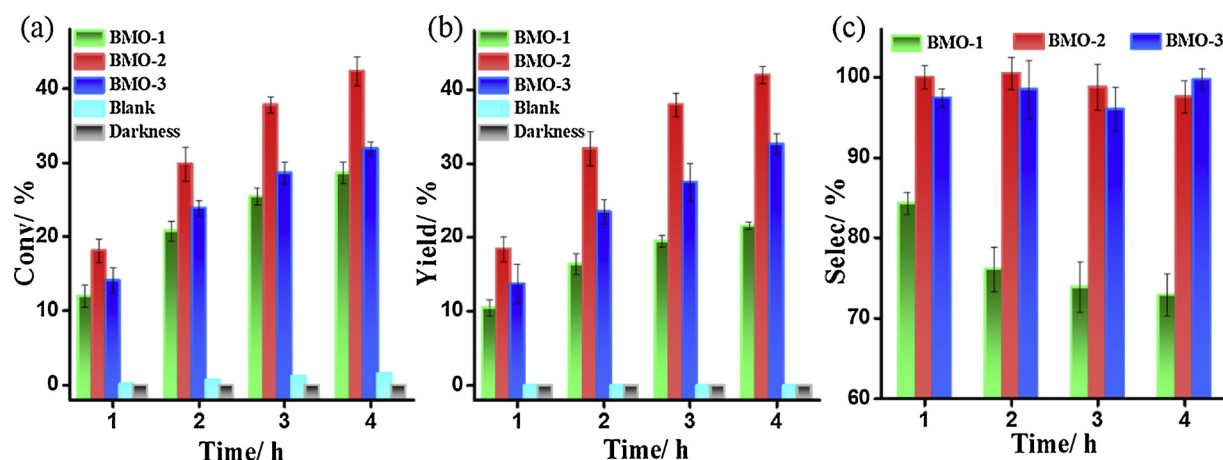


Fig. 2. The conversion (a), yield (b) and selectivity of photocatalytic glycerol oxidation to DHA (c) under visible light irradiation over **BMO** samples.

over-oxidize glycerol to glycolic acid, instead of DHA, under identical photocatalytic conditions, as shown in Figure S5 (Supporting Information). It further illustrates that the highest DHA yield of **BMO-2** in the photocatalytic oxidation of glycerol is ascribed to the large production of  $^1\text{O}_2$ .

To figure out the enhanced  $^1\text{O}_2$  generation in  $\text{Bi/Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$  heterostructure, photoluminescence experiments are performed to elucidate the energy transfer process in the production of  $^1\text{O}_2$ , which involves the spin-flip of triplet excitons [52,53]. The mean lifetimes calculated from the kinetics of the time-resolved fluorescence (PF) spectra is 3.13 and 2.57 ns for **BMO-1** and **BMO-2**, respectively (Fig. 4a). It indicates a more effective electron excitation from singlet to triplet in the **BMO-2** sample. And the stronger phosphorescence (PH) intensity of **BMO-2** also demonstrates its better photoactivation of triplet excitons than that of **BMO-1** (Fig. 4b). The steady-state fluorescence (PF) and phosphorescence (PH) spectra reveal that the energy gap between the singlet and triplet state ( $\Delta E_{\text{ST}}$ ) of **BMO-2** (0.183 eV) is much smaller than that of **BMO-1** (0.314 eV) (Fig. 4c). On the other hand, the time-resolved phosphorescence (PH) spectra illustrate the

longer average PH lifetime of **BMO-1** (144.60  $\mu\text{s}$ ) than that of **BMO-2** (68.85  $\mu\text{s}$ ), which implies a stronger spin-orbit coupling (SOC) of **BMO-2** (Fig. 4d). Based on the Franck-Condon principle, the energy transfer rate is mainly determined by the energy gap ( $\Delta E_{\text{ST}}$ ) and spin-orbit coupling (SOC) between singlet and triplet states [54]. Therefore, the reduced  $\Delta E_{\text{ST}}$  and enhanced SOC of **BMO-2** facilitates the energy transfer process and favors the efficient  $^1\text{O}_2$  generation. It is also found that the oxygen vacancy in **BMO** sample plays significant role in the generation of  $^1\text{O}_2$ . As shown in Fig. 4e, the solid electron paramagnetic resonance (EPR) signals with g-value of 2.00 are observed in the EPR spectra of **BMO-2**, which is attributed to the Zeeman Effect of single electron trapped by oxygen vacancies. The high resolution O 1s XPS spectrum of **BMO-2** sample (Fig. 4f) also reveals an obvious shoulder peak located at 532.1 eV, which is associated with  $\text{O}^{2-}$  ions in the oxygen deficient regions (ODR) [55]. To further confirm the function of oxygen vacancy in the generation of  $^1\text{O}_2$ ,  $\text{Bi/Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$  nanoparticles without oxygen vacancies (**BMO-5**) was also prepared and characterized (Figure S6, Supporting Information). The  $^1\text{O}_2$  production ability of **BMO-5** was determined by using the chemical trapping probe

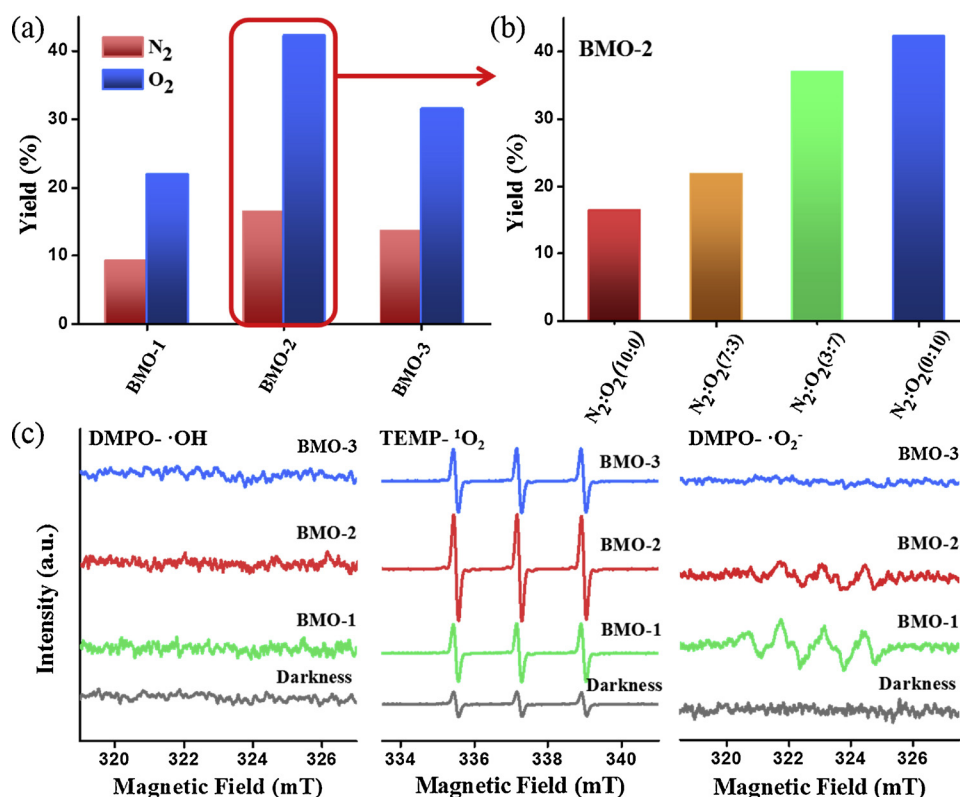
Table 2

Summary of the results of catalytic oxidation of glycerol.

Entry	Catalyst	Catal. Amt.	GLY Conc.	Time /h	Oxidation method	Temp./°C	Conv. /%	Selectivity / %						Ref.
								GAD	DHA	GCA	LA	GCOA	FA	
1	$\text{Bi/Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$	3.3*	6 <sup>a</sup> *	4	125 W Xe lamp	25	42.3	—	97.6	—	—	—	—	This work
2	Degussa P25	0.2*	9.2 <sup>a</sup> *	24.5	125 W Hg lamp	25	35	7	4	—	—	—	3	[15]
3	$\text{TiO}_2$	1*	1.84 <sup>a</sup> *	4	300 W Xe lamp	80	20	—	—	—	—	49	—	[29]
4	ZnO	2.5*	0.276 <sup>a</sup> *	1	125 W Hg lamp	40	36.2	39.3	17.7	—	—	—	—	[39]
5	$\text{TiO}_2\text{-H}_2\text{O}_2$	3*	2.76 <sup>a</sup> *	8	120 W Hg lamp	—	71.42	—	0.39	19.61	—	—	—	[14]
6	$\text{TiSi}_2$	10*	100 <sup>a</sup> *	12	300 W Xe lamp	65	97.6	—	—	100	—	—	—	[40]
7	$\text{Na}_4\text{W}_{10}\text{O}_{32}/\text{SiO}_2$	8*	0.92 <sup>a</sup> *	2	> 290 nm	25	16	59.4	5.6	5.3	—	—	—	[25]
8	7.5 wt.% Au/ $\text{TiO}_2$	1*	4.6 <sup>a</sup> *	15	> 420 nm	90	48	8	50	—	—	5	—	[30]
9	$\text{Bi}_2\text{WO}_6$	5.3*	0.046 <sup>a</sup> *	12	> 420 nm	25	90	—	93	—	—	—	—	[26]
10	5 wt.% Pd/ $\text{TiO}_2$	25*	46 <sup>a</sup> *	18	450 W Xe lamp	25	19	17	9	—	—	30	3	[41]
11	0.5% Au/ $\text{TiO}_2$	1:40‡	55.2 <sup>a</sup> *	4	Metal catalysis	60	54	—	—	30	—	40	—	[42]
12	2 wt.% Pd-Bi/C	2.5*	50 <sup>a</sup> *	4	Metal catalysis	200	1.8	33.1	54.1	10.1	—	—	—	[43]
13	2 wt.% AuPd/ $\text{TiO}_2$	2500‡	46 <sup>c</sup> *	4	Metal catalysis	140	25.5	—	8.3	5.4	—	2.4	2.6	[44]
14	0.64 wt.% Pt/HT	2500‡	9.2 <sup>a</sup> *	24	Metal catalysis	90	54	74	—	—	—	—	—	[45]
15	AuPt(1:3)/MgO	500‡	27.6 <sup>a</sup> *	24	Metal catalysis	25	29.7	—	—	66.7	—	11.5	12.6	[46]
16	1%Bi-5%Pt charcoal	5*	100 <sup>a</sup> *	4	Metal catalysis	50	30	—	20	—	—	—	—	[24]
17	NCNTs800	5‡	1380 <sup>b</sup> *	6	Metal catalysis	60	8.3	—	73.8	—	—	—	6.5	[5]
18	$[\text{Cp}^*\text{Ir}(\text{Ime})_2\text{Cl}]\text{BF}_4$	143‡	1 <sup>a</sup> †	15	Metal catalysis	115	4.5	—	—	—	95	—	—	[21]
19	$[\text{Ir}(\text{COD})(\text{Ime})_2]\text{BF}_4$	500‡	Neat <sup>a</sup>	40	Metal catalysis	115	50	—	—	—	0.98	—	0.01	[21]
20	TEMPO	0.0075 <sup>#</sup>	4.6 <sup>d</sup> *	20	Electro-catalysis	—	25	—	100	—	—	—	—	[23]
21	PtSb/C	—	9.2 <sup>a</sup> *	10	Electro-catalysis	60	95.8	—	35.4	—	—	—	—	[47]
22	<i>C. pasteurianum</i>	—	75–90 <sup>*</sup>	25	Microbial fermentation	—	77.4	—	—	—	25	—	—	[48]

Reaction conditions: <sup>a</sup>  $\text{H}_2\text{O}$  <sup>b</sup> TPBH (70% in water) <sup>c</sup>  $\text{AlCl}_3$  (10 mmol  $\text{L}^{-1}$  in water). <sup>d</sup>  $\text{Na}_2\text{CO}_3$  (0.2 M) Unit: \* g/L. ‡ glycerol/metal (mol/mol). † glycerol/catalyst (wt:wt). † glycerol/water (V: V). # mol/L.





**Fig. 3.** The DHA yield of photocatalytic glycerol oxidation over **BMO-2** in the presence of saturated N<sub>2</sub> and O<sub>2</sub> atmosphere (a), different proportion of N<sub>2</sub>/O<sub>2</sub> gas mixture (b) and ESR spectra of DMPO-·OH, TEMP-<sup>1</sup>O<sub>2</sub> and DMPO-·O<sub>2</sub><sup>-</sup> of **BMO** samples (c).

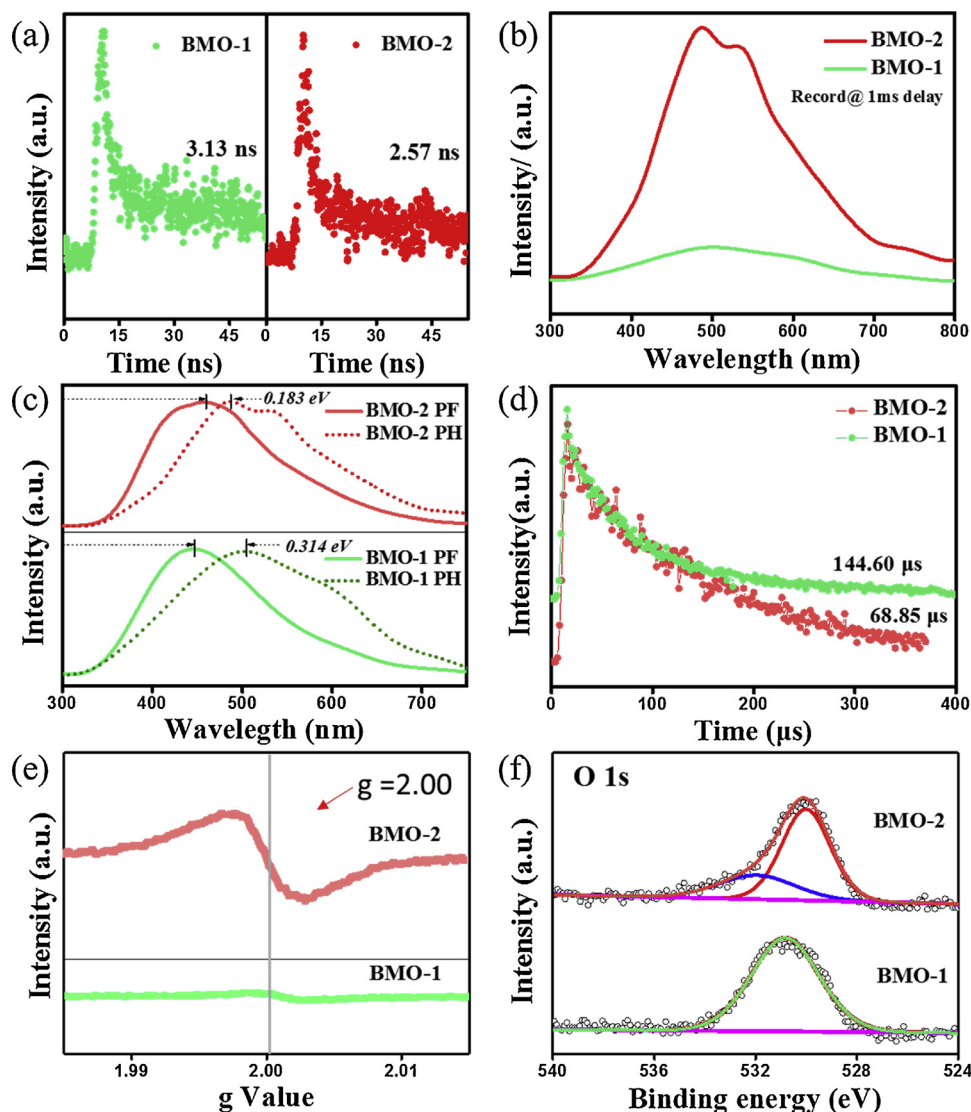
(DPBF), compared with **BMO-2** and **BMO-1**. (Figure S7, Supporting Information). The decay rate of DPBF in the presence of **BMO-2** was significantly larger than that of **BMO-5**, which displays equivalent <sup>1</sup>O<sub>2</sub> production ability with **BMO-1**. It illustrates that the generation of oxygen vacancies in **BMO-2** sample promoted the generation of <sup>1</sup>O<sub>2</sub>. In the reported literatures, oxygen vacancies could form oxygen vacancy states lying close to the conduction band of the photocatalyst, which were likely to affect the energy gap in the sample [56]. Hence, it is proposed that the oxygen vacancies in **BMO-2** sample could form a new energy state below the conduction band to decrease the energy gap, thus enhancing the triplet-exciton yield by synergistically promoting intersystem-crossing and reducing the singlet-triplet energy gap of the matrix, and facilitating the <sup>1</sup>O<sub>2</sub> generation through the energy transfer process. This is also in accordance with our previously reported work [51].

In this work, although it is found that the photogenerated electrons is extremely important for the generation of ROS in the photocatalytic oxidation of glycerol, the photogenerated holes also greatly contribute to the selective oxidation of glycerol to DHA. As confirmed by the scavenge experiments, the DHA yield dramatically decreases from 42% to 25% over **BMO-2** with the addition of AO (hole scavenger) (Figure S8, Supporting Information), implying that the photogenerated holes also contribute to the selective oxidation of glycerol to DHA. It is well known that the generation of metal-semiconductor junction might improve the migration efficiency of photogenerated carriers and suppress the recombination of hole-electron effectively, which would highly affect the hole generation process. Hence, electrochemical impedance spectroscopy (EIS) was performed to investigate the separation efficiency of the photogenerated carriers. Compared with the pure Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> (**BMO-1**), **BMO-2** presents the smaller arc radius, suggesting the superior separation efficiency of the photoinduced electron-hole and the charge transfer (Figure S9a, Supporting Information). The transient photocurrent response of **BMO** samples also reveals that **BMO-2** enhances the photocurrent density significantly,

compared with **BMO-1** (Figure S9b, Supplementary Data). It illustrates that the metallic Bi could promote the separation of photogenerated carriers on Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> and facilitate the generation of hole. However, the photocurrent density of **BMO-3** decreases due to the shielding effect of the excessive Bi nanocrystals on the surface [35,38,57].

The potential of photogenerated holes in Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure is no doubt significant in the selective oxidation of glycerol to DHA which was determined by Mott-Schottky plots and valence band XPS spectra (Fig. 5a). The calculated band potential of Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> is -0.33 and 2.10 eV vs NHE for the conduction and valence band, respectively. Moreover, the redox potentials of glycerol and DHA are evaluated by the cyclic voltammetry in different concentrations (1 and 2 mM). As illustrated in Fig. 5b, the redox potential is estimated to be 1.78 and 2.02 eV vs Hg/Hg<sub>2</sub>Cl<sub>2</sub> (i.e., 2.02 and 2.26 eV vs NHE) for glycerol and DHA, respectively. Theoretically, the photogenerated holes could oxidize glycerol to produce glyceraldehyde or DHA via two pathway. The oxidation of primary hydroxyl group of glycerol results in the production of glyceraldehyde, and the oxidation of secondary hydroxyl group is more favorable for the generation of DHA. However, in this work, only DHA was obtained. Therefore, owing to the geometrical effect, the coordination of glycerol with the surface of catalyst is critical in the selectivity of the oxidation of glycerol [58,59]. To investigate the influence of the combination of glycerol on the surface of the Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> during the selective oxidation process, FT-IR spectra of **BMO** samples before and after glycerol adsorption are recorded.

As shown in Fig. 5c, the intensity of the absorption peak corresponded to glycerol (994, 1043, 1110, 2882 and 2936 cm<sup>-1</sup>) from Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure (**BMO-2** and **BMO-3**) is remarkably stronger than that of pure Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> (**BMO-1**) after adsorption-desorption equilibrium in glycerol solution. Moreover, the absorbed glycerol increases with the increase of Bi content in Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure, illustrating that bismuth function as adsorption sites to facilitate the surface complexation with glycerol. To



**Fig. 4.** Time-resolved PF kinetics (excitation at 275 nm) (a), PH spectra (delay time 1 ms, excitation at 275 nm) (b), the normalized steady-state PF and PH spectra (c), time-resolved PH kinetics (excitation at 275 nm) (d), EPR spectra (e) and High-resolution O 1 s XPS spectra (f) of BMO-1 and BMO-2 samples.

further understand the binding mode of Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> with glycerol, 1, 2-propylene glycol and 1, 3-propylene glycol are instead of glycerol to perform the FT-IR spectra of BMO samples after adsorption, respectively. It is observed that the peak intensity of adsorbed 1, 2-propylene glycol is proportional to the bismuth content. However, the content of Bi in Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure exhibits negligible influence on the adsorption of 1, 3-propylene glycol (Figure S10, Supplementary Information). Fig. 5d shows that the correlation between the Bi content and the relative polyol adsorption amount, and the calculated correlation coefficient is 0.9466, 0.9353 and 0.3828, respectively. Hence, the interaction mode of the glycerol and its derivatives with Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> is proposed in Fig. 5e. It illustrates that the metallic Bi in Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> facilitates the complexation of bismuth with ortho-hydroxyl in glycerol, which is beneficial for the selective oxidation of glycerol to produce DHA. Based on the results, it is evident that Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> could selectively oxidize glycerol to DHA via dual reaction pathways, which is illustrated in Scheme 1.

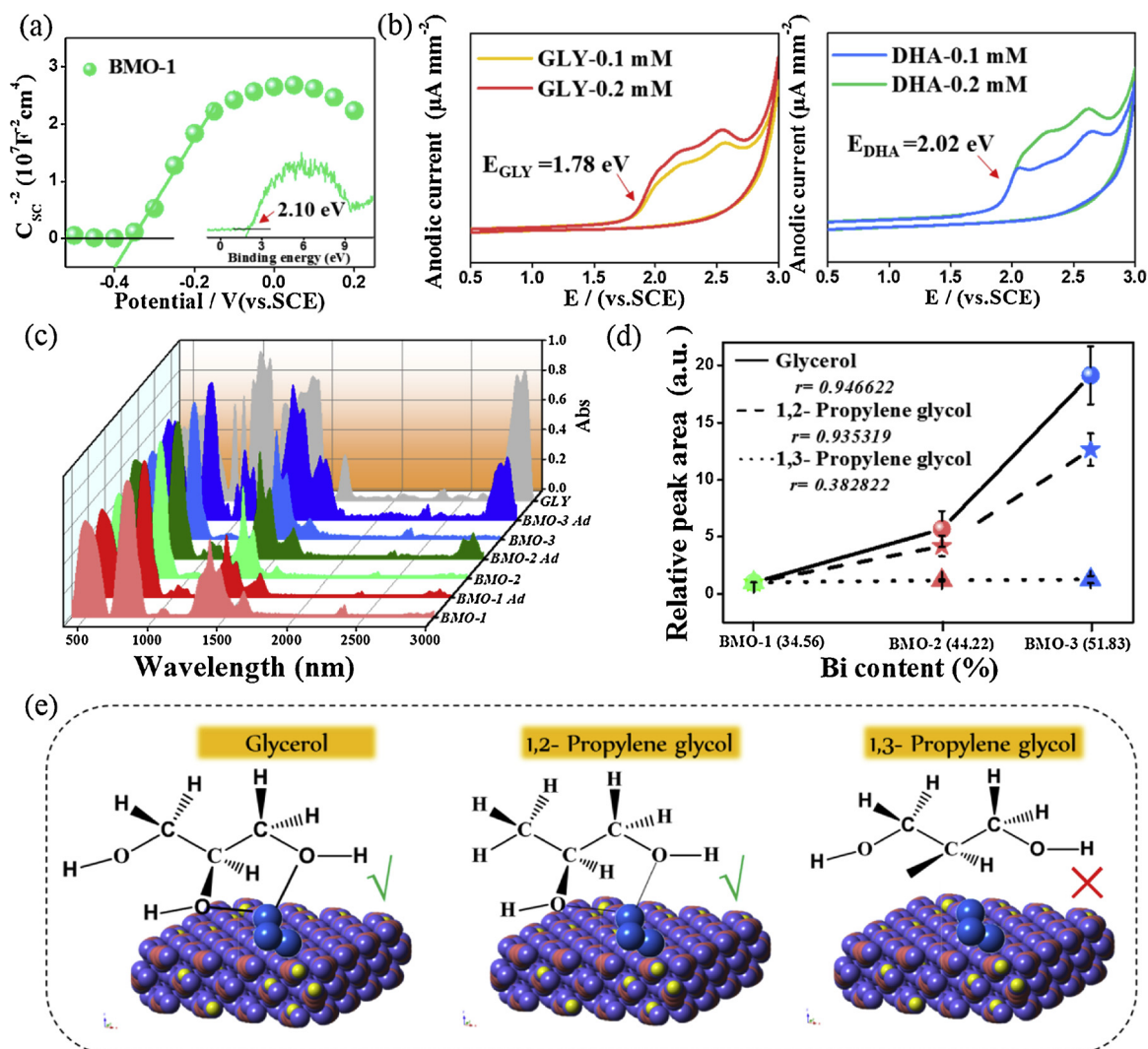
#### 4. Conclusions

In summary, the Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure have been successfully synthesized via a facile solvothermal method, which

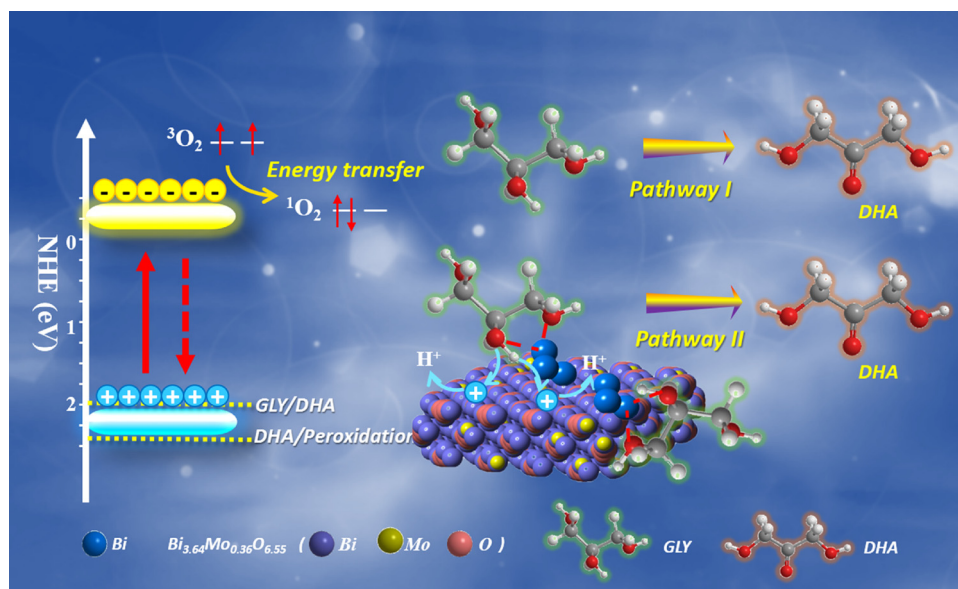
displays remarkable photocatalytic ability for selective glycerol oxidation to DHA under visible light irradiation. Moreover, the deep understanding of the high selectivity of Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure for photocatalytic oxidation of glycerol is discussed. The reduced energy gap ( $\Delta E_{ST}$ ), enhanced spin-orbit coupling (SOC) and the presence of oxygen vacancies in Bi/Bi<sub>3.64</sub>Mo<sub>0.36</sub>O<sub>6.55</sub> heterostructure favors the generation of dominated <sup>1</sup>O<sub>2</sub> reactive oxygen species. On the other hand, the metallic bismuth promotes the separation of photo-generated carries and the generation of holes with efficient redox potential for glycerol oxidation, and the coordination of bismuth with ortho-hydroxyl in glycerol facilitates the selective oxidation to DHA. The dual-pathway reaction process greatly promotes the selective oxidation of glycerol to DHA simultaneously. This work paves the way for the development of highly efficient heterostructured photocatalysts for selective oxidation.

#### Notes

The authors declare no competing financial interest.



**Fig. 5.** Mott-Schottky plots and band XPS spectra (inset) of **BMO-1** (a), the cyclic voltammogram of glycerol and DHA with different concentrations (b), FT-IR spectra of glycerol and **BMO** samples before and after glycerol adsorption (c), the correlation between the Bi content and relative polyol adsorption amount (d), and schematic illustration of the proposed of the glycerol intermediate with **BMO** samples (e).



**Scheme 1.** Proposed photocatalytic reaction pathways of selective oxidation of glycerol to DHA over  $Bi/Bi_{3.64}Mo_{0.36}O_{6.55}$  heterostructure.



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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.11.047>.

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